

(12) UK Patent Application (19) GB (11) 2 263 709 (13) A  
(43) Date of A publication 04.08.1993

(21) Application No 9301654.1

(22) Date of filing 28.01.1993

(30) Priority data

(31) 04013212 (32) 28.01.1992 (33) JP

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(51) INT CL<sup>5</sup>

C23C 16/26, C30B 25/02 29/04

(52) UK CL (Edition L)

C7F FHE FP908 FP913 FP914 FP916 FP919 FQ902  
FR902 F809  
U1S S1645 S1914 S2084

(56) Documents cited

GB 2240114 A GB 2228745 A EP 0470644 A  
US 5006203 A

(58) Field of search

UK CL (Edition L) C7F FHB FHE FHX  
INT CL<sup>5</sup> C23C, C30B  
Online databases: WPI, CLAIMS

(54) Method for producing silicon nitride based members coated with synthetic diamond

(57) A method for coating a substrate formed of a silicon nitride based material with a film of synthetic diamond by a gas phase synthesis technique including a first step of applying a film of synthetic diamond to a thickness of 0.5 to 2.0  $\mu$  m at a temperature not higher than a temperature at which grain boundary components of the substrate volatilize, and a second step of applying a film of synthetic diamond to a thickness of 5 to 100  $\mu$  m at a higher temperature, which expedites synthesis of the film of synthetic diamond. The silicon nitride based material may be  $\text{Si}_3\text{N}_4$ , or a silicon of the formula  $\text{Si}_{1-z}\text{Al}_z\text{N}_{1.5-0.5z}\text{O}_z$  (where z is 0-4.2). The silicon nitride based material may contain sintering aids such as  $\text{ZrO}_2$  or  $\text{MgO}$ .

The product has excellent durability and long service life because the film has tight adhesion to silicon nitride substrate due to nondegradation of the glassy grain boundary phase. The member may be used in a cutting tool, an optical material or an electronic material.

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TITLE:

Method for producing silicon nitride based members with synthetic diamond

DESCRIPTION:Field of the Invention

This invention relates to a method for producing a silicon nitride based member coated by a film synthetic diamond. Such a member may be employed in a variety of cutting tools, such as tips, end mills, cutters or drills; or optical materials; or electronic materials, since it exhibits superior wear resistance, corrosion resistance and durability.

Definitions

The term "film of synthetic diamond" used herein represents a film made up of diamond, or a structure analogous to diamond such as diamond-like carbon, or a mixture thereof, fabricated by a synthetic process such as that involving plasma-enhanced vapour deposition. The synthetic diamond coating includes not only pure diamonds, usually in a polycrystalline state, but allows the presence of minor amounts of an analogous phase. The presence of diamond major phase can be determined through Raman scattering spectrum by a peak which is characteristic for the diamond at about  $1333\text{ cm}^{-1}$ .

The term "silicon nitride based material" herein represents those materials in which the major phase is silicon nitride or a phase analogous to silicon nitride such as solid solution thereof like Sialon, or a mixture thereof.

BACKGROUNDRelated Art

A film of synthetic diamond is superior in hardness, wear resistance, electrical insulating properties or thermal conductivity and hence is currently employed in, e.g.

cutting tools, optical materials or electronic materials. In order for a member coated with such film of synthetic diamond to be used as a cutting tool for a prolonged period of time, it is necessary to have a good adhesion between the synthetic diamond and the substrate surface.

For this reason, it has been proposed in, for example, JP Patent KOKOKU Publication No. 60-59086 and JP Patent KOKAI Publication No. 63-306805, to employ a substrate consisting of a sintered body of ceramics, such as silicon nitride, a hard material which has a thermal expansion coefficient approximate to that of diamond and on which the film of synthetic diamond can be directly applied easily.

Silicon nitride has a thermal expansion coefficient approximate to that of diamond and is used as a sintered substrate with the least risk of peeling off of a diamond film deposited thereon under thermal stress which occurs subsequent to diamond coating. However, since silicon nitride can be sintered only with difficulty, sintering aids are added thereto. These sintering aids remain as a glassy phase in the grain boundary after sintering of silicon nitride ceramics.

The glassy phase in the grain boundary has in the past been exposed to the high-temperature plasma atmosphere which is used for synthesizing the diamond film on the substrate and is thereby volatilized. Such volatilization is mainly responsible for the ease of peeling off of the film of synthetic diamond from the substrate.

In JP Patent Application No. 2-406931 (now JP Patent Kokai No. 3-290383 laid open Dec. 20, 1991), one solution has been achieved in producing a member coated with a strongly adherent film of synthetic diamond by first

subjecting a silicon nitride based sintered body having the abovementioned glassy phase to a crystallization process followed by depositing a coating of synthetic diamond on the crystalline grain boundary phase of the resulting sintered body. However this solution increases the number of operating steps and hence production costs, which is counted as a drawback.

It is therefore a primary object of the present invention to provide a novel method which eliminates the aforementioned drawback.

Concretely, it is therefore an object of the present invention to provide a method for producing a silicon nitride based member which, since silicon nitride based ceramics may be freely selected so as to be used as a substrate to be coated with a film of synthetic diamond can be employed for a variety of cutting tools, a variety of protective films, optical materials or electronic materials, and which is excellent in wear resistance, corrosion resistance, and durability.

#### The Invention

According to the present invention, there is provided a method for coating a substrate formed of a silicon nitride based material with a film of synthetic diamond by a gas phase synthesis technique comprising

a first step of applying a first coating of synthetic diamond at a temperature not higher than a temperature at which the grain boundary components of the substrate volatilize, the film being applied to a thickness which is sufficient to suppress volatilization of the grain boundary phase components of the substrate during a subsequent step and

a second step of applying a second coating of synthetic diamond over the first coating at a higher temperature. The second coating is preferably applied to

a thickness sufficient to give desired characteristics such as wear resistance to a resulting product.

Because the first coating of synthetic diamond is applied at a temperature which does not volatilize the glassy phase in the grain boundary, strong adhesion is obtained between the substrate and that first coating. Furthermore that first coating is effective in protecting the glassy phase in the grain boundary of the substrate during application of the second coating.

In this manner, by diamond synthesis in the second step for providing wear resistance and corrosion resistance, the silicon nitride based member coated with synthetic diamond may be produced in which the glassy phase in the grain boundary phase of the substrate is not degraded and in which the synthetic diamond is difficult to peel off from the substrate. The resultant product is thus excellent in durability, operational performance, particularly as a cutting tool and economic effects due to simplified and yet expedited manufacturing.

#### Description of Preferred Embodiments

The synthesis temperature in the first step is preferably 700 to 900°C in the case where diamond is synthesized by a microwave plasma CVD method on a substrate comprising a Mg-containing silicon nitride based sintered body. In this case, if the temperature were lower than 700°C, the rate of diamond synthesis becomes significantly low with accompanying economic demerits. Temperatures higher than 900°C would cause the volatilization of the glassy phase.

The thickness of the synthetic diamond coating applied in the first step is preferably 0.5 to 2  $\mu\text{m}$ . If the thickness is less than 0.5  $\mu\text{m}$ , the effect of that coating in preventing volatilization of the glassy phase in the grain boundary of the substrate material in the second

step becomes poor, whereas, even if the thickness is larger than 2  $\mu\text{m}$ , the effect in preventing volatilization is not improved further.

The reaction time and reaction temperature in the first step will otherwise be chosen depending on the components of the base material and reaction gases.

The synthesis temperature in the second step is preferably 950 to 1200°C, more preferably about 1000 to 1100°C, so long as other conditions are substantially the same. If the temperature is lower than 950°C, the diamond synthesis rate is lowered with accompanying economic demerits. If the temperature exceeds 1200°C, the graphite structure becomes more stable than the diamond, so that the diamond synthesis rate is lowered.

It should be noted, however, that the film growth rate depends not only on the temperature, but other factors such as the gas pressure, and particularly the partial pressure of the carbon source gas. Optimum conditions for the second step may be selected from various known conditions for synthesizing diamond coatings or films. The temperature control of the substrate can be made without changing the gas conditions, and thus is a useful control parameter in the commercial production.

The thickness of the synthetic diamond coating applied in the second step is preferably 5 to 100  $\mu\text{m}$ . If it is thinner than 5  $\mu\text{m}$ , the effect in improving wear resistance by diamond coating of the substrate becomes insignificant. If it exceeds 100  $\mu\text{m}$ , the process becomes uneconomic, with insufficient further improvements in wear resistance.

As for the reaction time, reaction pressure and other conditions in the second step, generally it suffices if

they satisfy the known conditions for efficient formation of synthetic diamond films or coatings.

As to the substrate material, the silicon nitride based material may be a sintered body of silicon nitride and/or Sialon as a major phase with a grain boundary phase usually in a glassy state but optionally with a grain boundary phase in a partly or substantially crystallized state. It should be noted that the present invention permits the presence of a glassy boundary phase.

Typically, the silicon nitride based material may be a sintered ceramic body comprising  $\text{Si}_3\text{N}_4$  crystal grains as a major phase, or a Sialon (preferably of  $\beta$ -type) generally expressed by  $\text{Si}_{6-z}\text{Al}_z\text{N}_{8-z}\text{O}_z$  (where  $z$  is 0 to 4.2). The Sialon is a ceramic having a major phase of a solid solution formed of  $\text{Si}_3\text{N}_4$  with Al and oxygen. The major phase is usually at least 50 wt%, preferably 60 to 90 wt%, or more.

The silicon nitride based materials may be produced using sintering aids which generally form the boundary phase. The sintering aids include compounds of Al, Si, Y, Zr, Mg, rare earth elements and the like, such as oxide, nitride, carbide, boride, or complex compounds thereof. Preferred are oxides of those elements usually in combination of two or more compounds.

The silicon nitride based substrate materials can be produced by known methods, namely, starting materials are mixed, formed (or molded) and sintered at, e.g. 1500-2000°C, preferably 1600-1800°C. The substrate is usually ground and/or polished before the synthetic diamond deposition, usually to a surface smoothness equivalent to a tip of commercial grade.

To produce the coating of synthetic diamond, a gas phase

synthesis technique may be employed. Generally, it comprises so called vapor deposition technique such as physical vapor deposition or chemical vapor deposition. Preferred are techniques in which carbon is supplied from a carbon source and energized into a plasma gas to be deposited on a substrate. The presence of hydrogen is preferred to inhibit the deposition of amorphous carbon or graphite. The carbon source may be a hydrocarbon or carbon monoxide.

For energizing gas materials, generally plasma CVD technology is preferred, e.g, microwave plasma, RF plasma, DC plasma, magnetic plasma, thermal plasma etc. Most preferred is microwave plasma CVD (ones under magnetic field, too).

The temperature for the first step and the second step is specifically selected according to the invention. The atmosphere conditions of the film synthesis may be selected from the known range, usually under the evacuated pressure. Several tens to about 100 Torr would give satisfactory results.

The film growth rate of diamond is dependent of the temperature around 900-1000°C which is known in the art, e.g. Fig. 4 (p. 108) T. Ito et al, Science and Technology of New Diamond, pp 107-109, KTK Scientific Publishers. An expedited film growth rate is achieved usually at 950°C or above under the condition of CO and H<sub>2</sub> atmosphere in the microwave plasma CVD method.

For further details of the various conditions of the diamond film synthesis reference is made to the above article of T. Ito et al.

The film growth rate in the second step should for economic reasons, be substantially greater than the first



step, e.g. at least by a factor of 1.3, preferably by 1.5, more preferably by about 1.8 or more, most preferably 1.9 or more. In the first step, the film growth rate should be moderate so as to provide a first adhesion to the substrate and sufficient and uniform coverage over the entire surface including the grain boundary phase without deteriorating the grain boundary phase. In this regard, it should be noted that there is no specific limitation in the film growth rate so long as the requirements for the first step are satisfied.

## EXAMPLES

### Example 1

5 wt% each of zirconium oxide ( $\text{ZrO}_2$ ) and magnesium oxide ( $\text{MgO}$ ), as sintering aids, having specific surface area (BET) of  $5\text{m}^2/\text{g}$  and about  $10\text{m}^2/\text{g}$ , respectively, the balance being silicon nitride ( $\text{Si}_3\text{N}_4$ ) of average particle size  $0.7\mu\text{m}$  (BET  $10\text{m}^2/\text{g}$ ), were mixed together in a ball mill for 16 hours, and subsequently sintered in a pressurized nitrogen gas under a pressure of 80 atm at  $1800^\circ\text{C}$  for 2 hours. The resulting sintered body was processed by grinding with a diamond grinding wheel to produce silicon nitride ceramics equivalent to a cutting tip SPGN 421 having a surface roughness of  $14\mu\text{m}$  RMS ( $R_{\text{max}} 1.0\mu\text{m}$ ).

This tip was set as a substrate in a reaction vessel of a microwave plasma CVD apparatus. Reaction was carried out for one hour under conditions of a substrate temperature of  $900^\circ\text{C}$  and a pressure within the reaction chamber of 50 Torr, with a feed gas flow rate into the reaction chamber being set to 20 SCCM for carbon monoxide gas and to 80 SCCM for hydrogen gas, respectively, and with a microwave output set to 300 W, for forming the diamond on the substrate to a

thickness of  $1\text{ }\mu\text{m}$  (, i.e., at a film growth rate of  $1\text{ }\mu\text{m/hour}$ ) (first step).

Subsequently, the substrate temperature in the microwave plasma CVD apparatus was further raised to  $1,000^{\circ}\text{C}$ , and reaction was carried out for ten hours under otherwise the same conditions as described above for coating the substrate with a diamond film to an additional thickness of  $19\text{ }\mu\text{m}$  (, i.e., at a film growth rate of  $1.9\text{ }\mu\text{m/hour}$ ), that is to a total thickness of  $20\text{ }\mu\text{m}$ , to produce a sample of Example 1. (Second step)

In this Example, a temperature difference of  $100^{\circ}\text{C}$  between the first step and the second step provided sufficient difference in the film growth rate.

As a result of a Raman spectroscopic analysis of the coating film of Example 1, it was found that a peak ascribable to diamond was present in the vicinity of  $1,333\text{ cm}^{-1}$  of the Raman scattering spectrum so that the diamond in the film was substantially free from impurities.

Using the sample of Example 1, a cutting test was carried out under the following conditions:

Work:	aluminum alloy (containing 8 wt% of silicon)
Cutting speed:	800 m/min
Feed Rate:	0.1 mm/rev

Depth of cut:	0.25 mm
Coolant:	Dry

It was found that, after the cutting test for 30,000 m, there occurred no peeling off of the diamond film or abnormalities such as chipping.

#### Comparative Example 1

Using a substrate employed in Example 1, as a tip, reaction was carried out in a microwave plasma CVD apparatus under conditions of a substrate temperature of 1,000°C and a pressure within the reaction chamber of 50 Torr, with the feed gas flow rates being set to 20 SCCM and 80 SCCM for the carbon monoxide gas and for the hydrogen gas, respectively, and with the microwave output being set to 300 W, for coating the substrate with a diamond film of 20  $\mu$ m for producing a sample of Comparative Example 1. Meanwhile, the method of Comparative Example 1 corresponds solely to the second step of Example 1.

Using the sample of Comparative Example 1, a cutting test was carried out under the same conditions as those for Example 1.

As a result of the test, peeling off was seen to have occurred between the diamond film and the substrate after cutting 10,000 m. After the cutting test, the substrate side surface of the diamond film peeled off was

checked with a scanning electron microscope (SEM). It was found that substrate components were affixed to the diamond film surface thus indicating that film peeling off was incurred as a result of deterioration in strength of the corresponding substrate surface portion.

It is seen from above that the present invention provides a method for producing the silicon nitride based member coated with the film of diamond-and-the-like according to which the glassy phase in the grain boundary of the silicon nitride based material is protected by the first step to improve a tight adhesion characteristic of the film of diamond-and-the-like without accompanying volatilization of the glassy phase at the time of synthesis of the film of diamond-and-the-like in the second steps. The result is that a silicon nitride based member coated with the film of diamond-and-the-like may be produced which is excellent in durability, operational performance and economic effects.

#### Example 2

Another silicon nitride based substrate material is prepared using 71 wt%  $\text{Si}_3\text{N}_4$  power of 0.7  $\mu\text{m}$  average particle size, 11 wt%  $\text{Y}_2\text{O}_3$  powder of 2  $\mu\text{m}$  average particle size, 3 wt%  $\text{Al}_2\text{O}_3$  powder of 1  $\mu\text{m}$  average particle size, and 15 wt% TiN powder of 1  $\mu\text{m}$  average particle size, wet mixing in a ball mill, drying and compacting followed by sintering under normal pressure in a nitrogen atmosphere at 1700 °C for one

hour. Without subjecting to crystallization treatment of boundary phase, the resulting sintered body is further ground to a tip of a cutting tool shape SPGN 421 to a similar surface smoothness as Example 1, and then subjected to a first step of diamond synthesis at 950 °C otherwise under the same condition as in Example 1.

The resultant mass is further processed according to the method of the second step substantially equivalent to Example 1 resulting in a diamond-coated sample tip. This tip has substantially equivalent cutting performance to Example 1 when tested under the same condition as Example 1.

It should be noted that modification may be made without departing from the gist and scope of the present invention as herein disclosed and claimed in the appendent claims. Particularly the following general information can be considered in practising the present invention.

According to the foregoing embodiments, a silicon nitride having substantially glassy grain boundary phase was used as a substrate. However, it is noted that the present invention is not limited to such silicon nitride and can be applied to silicon nitride base substrate materials with various structures of the grain boundary phase, irrespective of the type and composition of the grain boundary phase.

As for the diamond synthesizing method, there are various known methods, generally classified in chemical

transport reaction method, thermal energization method, halogen promotion method and plasma energization method. Under the plasma energization method, microwave plasma method, high frequency plasma method and direct current plasma method are counted. In the plasma method, the substrate is heated through heat conduction from the plasma itself and induction heating. The film growth rate also depends on the gas pressure, generally amounting to 1  $\mu\text{m}/\text{hour}$  at a pressure of 100 Torr or less counted for one of the preferred methods, due to the stability for long operation, excellent reproducibility, low contamination of impurities from electrode materials because of its electrodeless discharge, in order to achieve a diamond film of high quality. For controlling the plasma, magnetic field can be applied. For expedite film growth, a higher pressure of 200 Torr or above may be used for stabilizing the plasma, under which argon (inert gas) may be mixed with carbon source (CO or hydrocarbon etc)

As for the temperature dependency of diamond growth rate, reference is made to M. Kamo et al, Proc. 2nd Int. Symp. Diamond Mater. The Electrochemical Soc. (1991) p. 20 under methane/hydrogen system; as well as E. Kondoh et al, Phys. Lett. 59 (1991) 488 under the thermal filament method.

The pressure under which the diamond-and-the-like is deposited generally ranges  $10^{-8}$  to  $10^3$  Torr, practically  $10^{-}$

° to 800 Torr. Preferably, the second step is carried out at a temperature of at least 50 °C (more preferably 100 °C) higher than that in the first step.



CLAIMS:

1. A method for coating a substrate formed of a silicon nitride based material with synthetic diamond by a gas phase synthesis technique comprising  
a first step of applying a first coating of synthetic diamond at a temperature not higher than a temperature at which the grain boundary components of said substrate volatilize, to a thickness which is sufficient to suppress volatilization of elements constituting grain boundary phase during a subsequent step, and  
a second step of applying a second coating of synthetic diamond at a higher temperature.
2. A method as defined in claim 1, in which the first step is carried out until the first coating is deposited with a thickness of 0.5 to 2.0  $\mu\text{m}$ .
3. A method as defined in either preceding claim, in which the second step is carried out until the second coating is deposited with a thickness of at least 5  $\mu\text{m}$ .
4. A method as defined in claim 3, in which the second step is carried out until the second coating is deposited with a thickness of 5 to 100  $\mu\text{m}$ .
5. A method as defined in any preceding claim, in which the first step is carried out at a temperature of 700-900°C.
6. A method as defined in claim 5, in which the substrate has a boundary phase comprising the elements Mg and/or Zr.
7. A method as defined in any preceding claim, in which the substrate has a glassy boundary phase.

8. A method according to any preceding claim, wherein the second step is carried out at a temperature at least 50°C higher than that in the first step.
9. A method according to claim 8, wherein the second step is carried out at a temperature at least 100°C higher than that in the first step.
10. A method as defined in any of claims 1 to 7, in which the second step is carried out at a temperature of 950-1200°C.
11. A method as defined in claim 10, in which the second step is carried out at a temperature of 1000-1100°C.
12. A method as defined in any preceding claim, in which the substrate is maintained at a temperature of 700-900°C during the first step.
13. A method as defined in any preceding claim, in which the substrate is maintained at a temperature of 950-1200°C during the second step.
14. A method as defined in any preceding claim, in which the first step is carried out at 900°C to form a synthetic diamond coating to a thickness of at least 1  $\mu\text{m}$ , and the second step is carried out at 1000°C to form a further synthetic diamond coating to a thickness of at least 5  $\mu\text{m}$ .
15. A method as defined in any preceding claim in which the second step is carried out to form a thickness of at least 19  $\mu\text{m}$ .
16. A method as defined in any preceding claim, in which the first and second steps are carried out through

microwave plasma CVD method in an evacuated atmosphere.

17. A method as defined in claim 16, in which said atmosphere comprises carbon monoxide gas and hydrogen gas.

18. A method as defined in any preceding claim, in which the second coating is synthesized at a higher growth rate than the first coating by a factor of at least 1.3.

19. A method as defined in claim 18, in which the second coating is synthesized at a higher growth rate than the first coating by a factor of at least 1.5.

20. A method as defined in claim 19, in which the second coating is synthesized at a higher growth rate than the first coating by a factor of at least 1.8.

21. A method as defined in claim 20, in which the second coating is synthesized at a higher growth rate than the first coating by a factor of at least 1.9.

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Application number

GB 9301654.1

Relevant T chnical fields

(i) UK Cl (Edition L ) C7F (FHB FHE FHX)

(ii) Int Cl (Edition 5 ) C23C; C30B

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Search Examiner

P G BEDDOE

Date of Search

26 APRIL 1993

Documents considered relevant following a search in respect of claims 1-21

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2240114 A (STC) see especially page 4 lines 4-29	1
X	GB 2228745 A (KABUSHIKI) see especially Claims 4, 5; Examples 2,3 (NB page 19 lines 19-22)	1,16
X	EP 0470644 A2 (NORTON) see especially Claims 1, 2; Example 1	1
X	US 5006203 A (TEXAS) see especially Claim 1; Figures	1,16

Category	Identity of document and relevant passages	Relevant to claim(s)

### Categories of documents

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**A:** Document indicating technological background and/or state of the art.

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